Utilization of Reverse Electrodialysis Processes for the Abatement of Pollutants in Water

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The simultaneous generation of electric energy and the treatment of waters contaminated by Cr(VI) was carried out by reverse electrodialysis processes using salinity gradients. The effect on the process of the nature of the cathode was investigated.

1. Introduction

Reverse electrodialysis is a clean, renewable energy with large global potential since the electricity is produced from supplies of water with different salt concentrations (Brauns, 2008; Pattle, 1954). In reverse electrodialysis (RED), cation and anion conductive membranes are placed in an alternating way in order to produce dilute and concentrate compartments (Post et al., 2008). The salt concentration difference (salt gradient) between both compartments in the cell pair creates a Nernst potential across the cell pair which causes an electrical current to flow through the electrical load connected to the electrodes (Veerman et al., 2010a). In order to convert this potential energy in electric energy by RED the following components are necessary (Scialdone et al., 2012; Scialdone et al., 2013):

(1) anion-exchange membranes (AEMs) and cation-exchange membranes (CEMs) used to selectively drive the flow of positive ions in one direction (toward the cathode) and the negatively charged ions in the opposite direction (toward the anode).
(2) solvents, which make a continuum for ion transport;
(3) electrolytes, i.e. the current carriers between cathode and anode;
(4) electrodes, where electron transfer reactions occur to allow the transformation of the charge carrier from ion to electron;
(5) end membranes to confine the special ions of the electrolyte;
(6) spacers, to ensure the feed of the stack with the low and high concentrated solutions.

It was shown that a proper selection of redox species and of electrode materials is of paramount relevance in order to develop the RED process on an applicative scale (Veerman at al., 2010b; Scialdone et al., 2012; Scialdone et al., 2013). Some authors recently studied the possible utilization of capacitive electrodes for RED processes (Vermaas et al., 2013). The group of Logan proposed the utilization of bacterial oxidation of organic matter to increase the energy capture in RED stack (Cusick et al., 2012) while our group proposed recently the possible utilization in the frame of RED of a redox process for the wastewater treatment, such as waters contaminated by Cr(VI).

Chromium compounds are widely used in metal plating, paints and pigments, leather tanning, textile dyeing, printing inks and wood preservation (Dhal et al., 2013). Significant amounts of waste waters containing chromium, as Cr(VI) and Cr(III), are discharged by industries. Trivalent chromium is relatively harmless and plays an essential role in biological processes, whereas hexavalent chromium is about 100–1,000 times more toxic (Cespon-Romero et al., 1996). It is limited in groundwater by a World Health Organization provisional guideline value of 0.05 mg/L. For wastewater in Italy a limit value of 0.2 mg/L is

fixed. Chemical and electrochemical reduction is an effective approach widely studied in literature (Barrera-Díaza et al., 2012; Lakshmipathiraj et al., 2008; Welch et al., 2005) for the treatment of such solutions. Direct electrochemical reduction of toxic Cr(VI) into the less toxic Cr(III) (which can be removed from solution via efficient precipitation in the form of $Cr(OH)_3$ hydroxide) on carbon electrodes (such as carbon felt or reticulated vitreous carbon) was studied in detail in the last years (Barrera-Díaza et al., 2012). As above mentioned, it has been recently proposed the utilization of reverse electrodialysis processes for the cathodic reduction of Cr(VI) to Cr(III), thus avoiding the necessity to supply energy to the system.

By this approach, it would be possible to overcome one drawback of electrolyses related to the need of using significant amount of electric energy. As an extension of this research, the electrochemical reduction of Cr(VI) in Cr(III) by RED process was here studied with the main aim to evaluate the effect of the nature of the cathode on the process.

2. Experimental

2.1 Electrolyses

The electroreduction of Cr(VI) was first studied in a two compartments glass cell divided by an anionic exchange membrane. The cathodic compartment contained a water solution (70 mL) of Cr(VI) (as $K_2Cr_2O_7$, Sigma-Aldrich), 0.1 M Na_2SO_4 (Sigma Aldrich) and H_2SO_4 (Sigma-Aldrich) to adjust the pH (pH = 2) stirred by a magnetic stir bar. Carbon felt (The Electosynthesis Co), compact graphite (Carbone Lorraine) or reticulated vitreous carbon (80ppi, Electrosynthesis Co) were used as cathode (geometric exposed area 5.5 cm^2) and a Saturated Calomel Electrode (SCE) as the reference electrode. The anodic compartment contained the same solution without Cr(VI). Titanium meshes of IrO_2-Ta_2O_5 (Magneto) were used as anode. Amel 2055 potentiostat was used for all the electrolyses. All experiments were repeated at least twice.

2.2 RED experiments

The stack consists of n anion and n+1 number of cation-exchange membranes (Fuji), gasket integrated with spacers (Guerreri et al., 2013) (Deukum, 0.28 mm thickness) and two external membranes to separate electrodic compartments and side ones, creating n pairs of alternating high concentrated (HC) and low concentrated (LC) chambers as previously described (Scialdone et al., 2013). A cationic (Nafion) and an anionic (Selemion) external membranes were used in contact with cathodic and anodic compartments, respectively. The two electrode chambers contained a carbon felt or a compact graphite cathode (Carbone Lorraine) and a titanium meshes coated with Ti/IrO_2-Ta_2O_5 anode (Magneto). The area of each electrode and of each membrane was 100 cm^2. Two peristaltic pumps (General Control SpA) continuously fed the HC and LC solutions. Two closed-loop hydraulic circuits were used for electrodic solutions (Scialdone et al., 2013). The two electrodic solutions were continuously recirculated to the electrodic compartments and to two different reservoirs by two peristaltic pumps (General Control SpA). During power density curve experiments, fresh HC and LC solution were pumped through the RED stack with the effluents collected in separate vessels.

Solutions used in HC and LC compartments were prepared by dissolving NaCl (analytical grade Sigma-Aldrich) into deionized water. Experiments were performed with two separated solutions flowing in the electrodic compartments:

• anodic solution containing 0.1 M Na_2SO_4 (Sigma-Aldrich) and H_2SO_4 (pH = 2)
• cathodic solution containing Cr(VI) (grade Sigma-Aldrich), 0.1 M Na_2SO_4 (grade Sigma-Aldrich) as supporting electrolyte at a pH = 2 (H_2SO_4).

2.3 Analyses

Experiments in the stack were performed using an external resistance (1 Ω) and measuring the current intensity by a multimeter Simpson. Power was calculated by multiplying the electrical current and the total cell voltage. Power density was computed by the ratio between the power and the geometric area of the electrode.

The removal of Cr(VI) was monitored by using Agilent Cary 60 UV Spectrophotometer. Cr(VI) was detected at λ = 540 nm, after treatment with 1,4-diphenylcarbazide and its concentration was determined after proper calibration using the Lambert Beer law. The lower detection limit for Cr(VI) was 0.01 ppm.
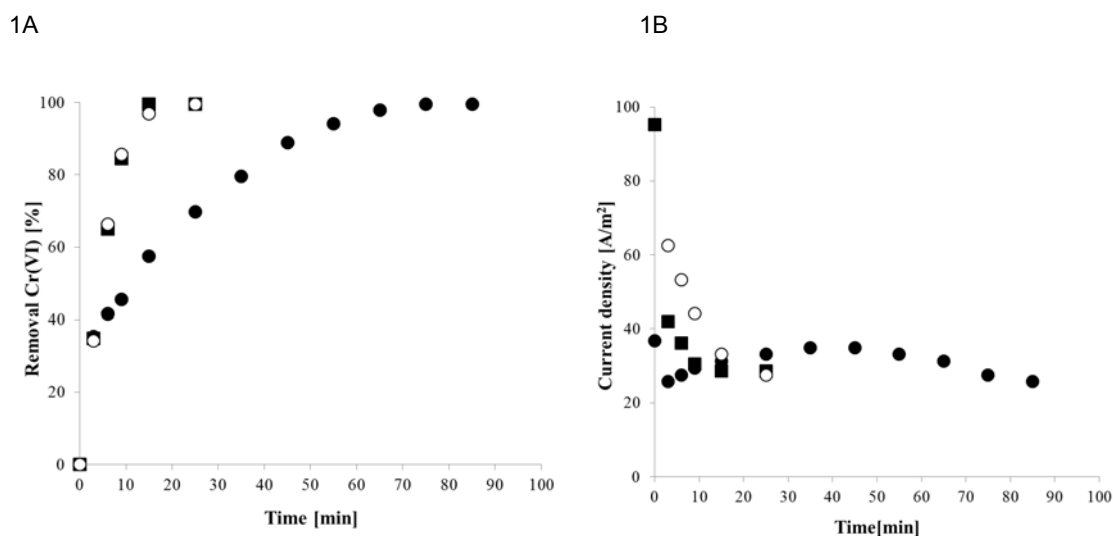
1A   1B

Figure 1: electrolyses performed in a two-compartments divided cell. Figure 1A reports the effect of the nature of the cathode material on the removal of Cr (VI) for potentiostatic experiments (-1.2 V vs. SCE) performed with carbon felt (■), reticulated vitreous carbon (o) and compact graphite (•). Figure 1B reports the current densities vs. time with carbon felt (■), reticulated vitreous carbon (■) and compact graphite (•).

3. Results and discussion

First experiments were carried out in a two compartment divided cell equipped with graphite, carbon felt or reticulated vitreous carbon cathode under a potentiostatic mode with a diluted water solution of Cr(VI) (2 ppm) loaded with Na_2SO_4 (0.1 M) as supporting electrolyte. According to the literature, the cathodic reduction of Cr(VI) to Cr(III) strongly depends on the pH of the solution (Wang et al., 2008; Frenzel, et al., 2006). Low pH gave higher rates for the removal of Cr(VI). This is probably due, at least in part, to the formation of a passivation layer of $Cr(OH)_3$ for pH higher than 2 (Welch et al., 2005; Roberts and Yu, 2002). Hence, we decided to work with an initial pH of 2 (by addition of H_2SO_4). A working potential of -1.2 V vs. SCE was initially used quite close to the reduction peak of Cr(VI) at carbon felt cathode of about -1 V evaluated by focused cyclic voltammetric experiments and by previous studies (Golub and Oren, 1989; Chaudary et al., 2003). As shown in figure 1, according to literature, the utilisation of a carbon felt cathode gave faster abatements (figure 1A) and higher current densities (figure 1B) with respect to that achieved at compact graphite cathode because of the higher active surface. Indeed, carbon felt presents a three-dimensional structure with dramatically higher surface with respect to the geometric one. Just slightly slower abatements of Cr(VI) were achieved when the carbon felt was replaced with reticulated vitreous carbon.

To evaluate the effect of the cathodic material on the removal of Cr(VI) achieved by RED, a series of experiments was carried out in a stack equipped with 40 or 50 cell pairs using carbon felt or compact graphite as cathode. A large number of cells was used to achieve not too low current densities. The stack was equipped with a $Ti/IrO_2\text{-}Ta_2O_5$ anode. Experiments were performed by feeding a water solution of Cr(VI) (25 ppm) and Na_2SO_4 with an initial pH of 2 in the cathodic compartment and a water solution of Na_2SO_4 in the anodic one. A salinity gradient similar to that expected for brine and seawater solutions was used (Tedesco et al., 2012; Guerreri et al., 2012): thus, the concentration of NaCl was 5 M and 0.5 M in the HC and LC compartments, respectively. Main reactions occurring in electrode compartments are detailed in the following:
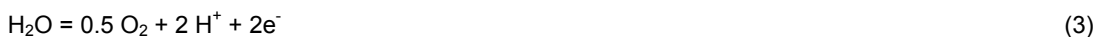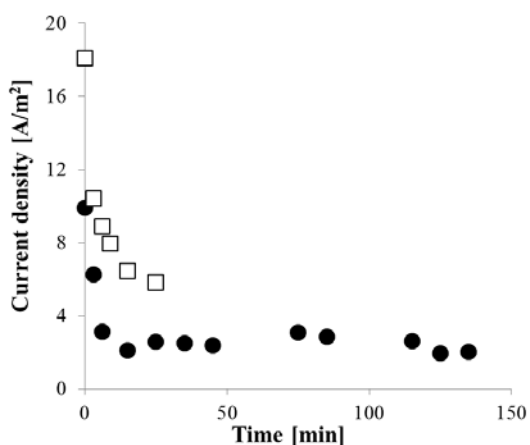
Cathode:
$$Cr(VI) + 3e^- \rightarrow Cr(III) \tag{1}$$

and/or

$$2 H_2O + 2e^- = H_2 + 2OH^- \tag{2}$$

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Anode:

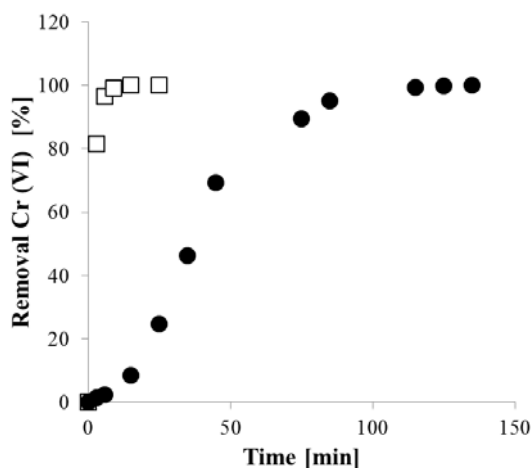$$H_2O = 0.5\ O_2 + 2\ H^+ + 2e^-$$
(3)

2A

2B

Figure 2: effect of the nature of the cathode material. Figure 2A reports the current densities vs. time and figure 2B reports the abatement of Cr(VI) achieved in a stack equipped with 50 cell pairs and carbon felt (□) or compact graphite (●) as cathode (100 cm^2). The cathodic solution contained 0.1 M Na$_2$SO$_4$ as supporting electrolyte. Anode: Ti/IrO$_2$-Ta$_2$O$_5$. Alimentations: NaCl 5 and 0.5 M in HC and LC, respectively. The cathodic solution contained Na$_2$SO$_4$ as supporting electrolyte at a pH = 2 (H$_2$SO$_4$) and Cr(VI) with an initial concentration of 25 ppm; the anodic solution contained Na$_2$SO$_4$ and H$_2$SO$_4$ (pH = 2). Flow rate of electrodic solutions: 75 mL/min; flow rate of HC and LC solutions: 190 mL/min.

As shown in figure 2A, first experiments carried out with compact graphite allowed to achieve the generation of electric energy. The current and the power densities were quite low and decreased during the experiment from 9.9 A/m^2 to 2.03 A/m^2 and from 1.02 W/m^2 to 0.03 W/m^2, respectively, as a probable result of the consumption of Cr(VI). Indeed, in the presence of a suitable concentration of Cr(VI), the cathodic process is given by the reduction of Cr(VI) to Cr(III) which requires a lower reduction potential with respect to the cathodic reduction of water which occurs in the absence of Cr(VI). As shown in figure 2B, the reverse electrodialysis allowed a drastic reduction of the concentration of Cr(VI). After 85 min the concentration of Cr(VI) decreased from 25 to about 1 ppm. After about 130 min, the concentration of Cr(VI) decreased below the detection limit (< 0.01 ppm), thus demonstrating that RED process can be used to treat waste waters contaminated by Cr(VI). In order to improve the performances of the process, the experiments were repeating using carbon felt as cathode. As shown in figure 2, the utilisation of a carbon felt cathode allowed to improve the process. Indeed, at carbon felt cathode, significantly higher current (from 18.1 A/m^2 to 5.82 A/m^2) and power densities (from 3.31 W/m^2 to 0.34 W/m^2) were achieved (figure 2A) with respect to that achieved at compact graphite cathode because of the higher active surface. Furthermore, a faster removal of Cr(VI) was achieved (Figure 2B) as a result of the higher current densities. After 17 min the concentration of Cr(VI) decreased from 25 to about 1 ppm. More relevant, just about 35 min were sufficient to decrease the concentration of Cr(VI) below the detection limit (< 0.01 ppm).

4. Conclusions

The effect of the nature of the cathode on the treatment of Cr(VI) by reverse electrodialysis processes was studied using carbon felt, reticulated vitreous carbon or compact graphite cathode. Preliminary electrolyses showed that the all adopted electrodes can allow the successfully reduction of Cr(VI) to Cr(III) even if the adoption of carbon felt gave the faster removal of Cr(VI). Consistently, the utilization of a carbon felt cathode allowed to achieve the simultaneous generation of electric energy and the treatment of waste waters contaminated by Cr(VI) by a reverse electrodialysis process using salinity gradients with the higher current densities and the faster abatements. However, a successfully treatment of waste waters contaminated by Cr(VI) was achieved by reverse electrodialysis also using a very cheap compact graphite cathode even if longer times were necessary.

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